Hydrogen production from formic acid vapour over a Pd/C catalyst promoted by potassium salts: Evidence for participation of buffer-like solution in the pores of the catalyst

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ABSTRACT

Doping a 1 wt.% Pd/C catalyst with alkali metal carbonates has a very significant promotional effect on its activity in hydrogen production from the decomposition of formic acid vapour (2 vol.%, 1 bar), potassium and caesium carbonates giving the largest effects. The K carbonate species present on the fresh catalysts react with formic acid to form formate ions, these being dissolved in a formic acid/water solution condensed in the pores of the support. The steady-state activities of the samples containing formate ions were 1–2 orders of magnitude greater than those of the unpromoted Pd/C and CO content was lower than 30 ppm. The activation energies for the reaction increased with doping from 66 to 88–99 kJ mol^{-1}, relatively independent of the cation of the dopant. Similar but lesser effects were found with unsupported Pd nanocrystals doped with K carbonate. The rate-determining step for the promoted samples appears to be the decomposition of formate ions on the Pd surface.

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1. Introduction

Although it is well-accepted that hydrogen has significant advantages as a fuel compared with petroleum or other fuels, there are still problems associated with its production, storage and transportation [1,2]. One solution for applications such as mobile fuel-cells is to produce the hydrogen in-situ by a reaction such as the steam reforming of methanol. However, this reaction has associated with the production of CO_2, a green-house gas. There would be a significant advantage if the hydrogen could be produced from a biomass-derived chemical since any CO_2 formed in parallel would be considered as a product of a carbon-neutral or "green" process. Hydrogen can be obtained by the gasification of biomass or bio-oil at high temperatures using catalysis [3,4] but this route is not easily applied to mobile systems. Potentially more valuable as a source of hydrogen is formic acid, a chemical that is formed as a by-product in the acid-catalysed hydrolysis of biomass [5,6]. Formic acid is easily handled and it can therefore be applied for hydrogen storage for transportation applications [7]. It is also worth noting that formic acid can be used directly as a hydrogen donor for hydrogenation

and deoxygenation reactions instead of molecular hydrogen [6,8,9]. A requirement for this application is that it would provide stable, CO-free hydrogen generation at low temperatures (<373 K). This demand can be achieved by careful choice of a catalyst and reaction conditions and a significant amount of work on the decomposition of formic acid is currently in progress aimed at finding suitable combinations. Hydrogen production from formic acid using heterogeneous catalysts has therefore been studied widely in both the liquid [10–14] and vapour [15–22] phases.

In the case of liquid phase decomposition of formic acid, Tedsree et al. [10] have reported that unsupported Pd nanoparticles have higher initial activities in the decomposition of formic acid than do nanoparticles of Rh, Pt, Ru, Au and Ag; however, they found that a catalyst consisting of Ag nanoparticles covered by a thin layer of Pd had the highest initial activity. Zhou et al. [11] investigated catalysts based on Pd–Ag and Pd–Au, each doped with ceria, and showed that the presence of Na formate gave a considerable improvement of the rate of hydrogen production; they found that the maximum values of turnover frequency (TOF) were about $0.06 \, s^{-1}$ at 365 K. Bi et al. [13] and Wang et al. [14], using Au/ZrO$_2$ and Pd/C catalysts, respectively, have published results confirming the promotion of the liquid-phase reaction by Na formate. Wiener et al. [23] have reported data on the decomposition of sodium formate over a heterogeneous Pd/C catalyst showing that the reaction occurs at low temperature (<373 K). Boddien et al. [24] demonstrated that

Table 1
Characterisation of Pd/C catalysts and kinetic parameters for the formic acid decomposition reaction.

Catalyst	M^+ content (wt.%)	M^+/Pd (mol mol^{-1})	Pd dispersion* (–)	T_{50} (K)	H_2 selectivity at T_{50} (%)	Activation energy (kJ mol^{-1})	Log(pre-exponential factor) (log(molecule s^{-1} gPd^{-1}))
Pd/C	0	0	0.38	385	98.9	66 ± 1	29.3 ± 0.1
Li-Pd/C	1.8	27	n/d	374	99.5	88 ± 4	32.7 ± 0.6
Na-Pd/C	5.6	27	n/d	355	98.8	99 ± 5	35.0 ± 0.3
2 K-Pd/C	2.0	5.4	0.257	367	99.6	98 ± 2	34.5 ± 0.4
5 K-Pd/C	5.0	13.5	n/d	347	99.8	n/d	n/d
10 K-Pd/C	10	27	0.245	340	99.8	97 ± 3	35.4 ± 0.5
20 K-Pd/C	20	54	n/d	342	99.8	87 ± 19	33.7 ± 3.0
Cs-Pd/C	34	27	n/d	344	99.9	92 ± 10	34.5 ± 1.7

n/d—not determined, *—determined by CO chemisorption, M^+—alkali metal ion.

hydrogen can be generated from different alkali metal formates dissolved in water at temperatures less than 373 K when catalysed by homogeneous Ru complexes.

For the reaction in the vapour phase, Solymosi et al. [21] found the following order of activity over a set of carbon-supported noble metals: Ir > Pt > Rh > Pd > Ru. Iglesia and Boudart [20] measured the activities of different supported Cu and Ni catalysts and reported that these gave decomposition at higher temperatures (>423 K) than did noble metal catalysts.

We have previously shown that a 1 wt.% Pd/C catalyst gave a TOF value of about 0.07 s^{-1} for the decomposition of formic acid at 373 K [15], this value being only slightly lower than that reported by Solymosi et al. [21] for an Ir/C catalyst (0.096 s^{-1}) under similar conditions. We have also recently demonstrated some preliminary results that showed that doping of the Pd/C and Pt/C catalysts with K carbonate had a significant promotional effect on the rate of formic acid decomposition [16]; this work was stimulated by reports that alkali metals have a strong promotional effect on the water–gas shift (WGS) reaction [25–28], the mechanism of which is probably closely related to that of formic acid decomposition [17,18,22]. Our results showed that the temperature required for formic acid decomposition was decreased to <353 K, the rate of hydrogen production being increased considerably (by 1–2 orders of magnitude) by doping with K carbonate. We interpreted our results by suggesting that K formate or bicarbonate species are formed at the K/C interface and that the spillover of these species gives rise to hydrogen formation at the Pd/C interface.

This paper gives more detailed results on the effect of the addition of the carbonates (or formates) of the alkali metals on the catalytic activity of the Pd/C catalyst for formic acid decomposition. Particular attention is paid to the initial stages of the reaction over the K carbonate promoted catalyst, the results showing that the formic acid reacts with K carbonate species to give formate ions that are dissolved in a formic acid/water solution condensed in the pores of the catalyst, thus forming a type of buffer solution; the subsequent decomposition of these formate ions on Pd particles to give hydrogen and CO_2 appears to be the rate determining step over these materials. The promotional effect seems therefore to arise from the presence of the formate ions in the buffer-like solution rather than being due directly to the presence of the alkali metal ions.

2. Experimental

Samples of the 1 wt.% Pd/C catalyst (Sigma-Aldrich) used previously [15,16] and of a Pd powder (Alfa Aesar) were used for the experiments reported here. Cs, K or Na carbonate or Li formate were deposited on these samples by incipient wetness impregnation using ultrasonic agitation; the preparation of the samples doped by K carbonate was described previously [16]. The resultant materials were dried at room temperature and then at 373 K. For simplicity, the sample compositions are expressed below in terms of the alkali metal ion contents despite the fact that we show below that the critical species in the reaction are the corresponding anions. The concentration of K ions was varied from 2 to 20 wt.%, this range corresponding to K/Pd mole ratios of 5.4:1 to 54:1 (Table 1). To allow comparison of the catalytic activities of all the supported catalysts, Pd contents of either 0.68 mg or 0.068 mg were used, these loadings being the same as those used in experiments with the undoped catalyst; for experiments involving the unsupported Pd powder, samples containing 6.8 mg of Pd were used, these being diluted with quartz grains to give a total bed weight of about 100 mg. The catalyst samples were placed in a fixed bed quartz reactor and were then reduced in a 1 vol.% H_2/Ar mixture for 1 h at 573 K followed by cooling in He to the reaction temperature. The concentration of formic acid vapour applied for the decomposition experiments reported below was 2.0 vol.%. The WGS reaction was studied with the following reaction mixture: 2.5 vol.% CO, 2.3 vol.% H_2O, balance He. The total flow rate of all the gas mixtures was 51 cm^3 min^{-1}. Further details of the procedures used are given elsewhere [15].

Turnover frequencies for the reactions were calculated from the rates determined at low conversions (<25%) making use of the corresponding Pd surface concentrations determined either from CO chemisorption measurements for the Pd/C catalysts or from the Brunauer–Emmett–Teller (BET) surface area determined for the Pd powder.

The BET surface areas of all the samples were measured by nitrogen adsorption using a Micromeritics Gemini system after pretreatment in a flow of nitrogen at 473 K for 2 h. Total pore volumes were determined using a Micromeritics ASAP 2010 system. CO chemisorption was performed using a Micromeritics AutoChem 2910 system. For the CO adsorption measurements, the Pd/C samples were heated to 573 K in a 5 vol.% H_2/N_2 mixture at a rate of 10 K min^{-1} and kept for 1 h at this temperature; they were then maintained in a flow of He at the same temperature for 1.5 h before cooling to 323 K and performing the pulse CO chemisorption measurements; a stoichiometric factor of 1.67 was used for the calculation of the dispersion [29].

Transmission electron microscopy (TEM) images and energy dispersive X-ray spectroscopy (EDS) data were obtained for the catalysts using a JEOL JEM-2100F (200 kV) microscope. X-ray photoelectron spectroscopy (XPS) was performed with a Kratos Axis 165 spectrometer using monochromatic Al $K\alpha$ radiation ($h\nu$ = 1486.58 eV) and a fixed analyser pass energy of 20 eV; the binding energy scale was referenced against the C 1s line (284.8 eV). X-ray diffraction measurements (XRD) were performed using a Philips X'Pert Pro MPD diffractometer equipped with Ni-filtered Cu $K\alpha$ radiation (λ = 1.5418 Å). Time-of-flight secondary ions mass spectrometric analysis (TOF-SIMS) was carried out with a TOF-SIMS 5 instrument (ION-TOF GmbH) using 30 keV Bi^{3+} primary ions; the target current used for surface imaging was equal to 0.11 pA and for spectrometry—0.35 pA.
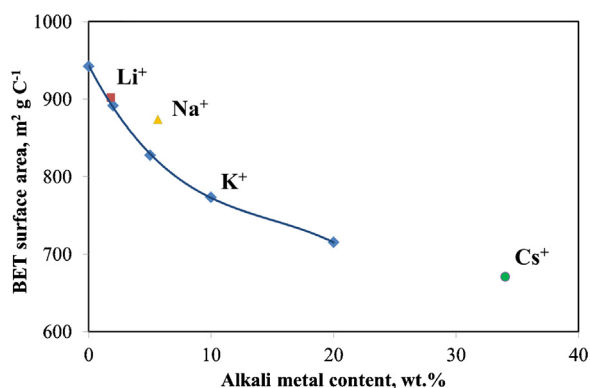
Fig. 1. The effect of the addition of alkali metal species on the BET surface areas expressed per gram of carbon support.

Fig. 2. Line scanning EDS/TEM of the 10 wt.% K–Pd/C catalyst.

3. Results

3.1. Characterisation of the catalysts

A number of the Pd/C samples doped with alkali metal carbonates or formates were characterised using BET surface area and CO chemisorption measurements. Fig. 1 shows the BET surface areas of the K-Pd/C samples plotted as a function of the amount of K (in the form of carbonate) added and also shows the BET areas of the samples doped with the other alkali metal salts (all carbonate except for Li formate) with a constant molar ratio of 27 of alkali metal to Pd. The BET surface area of the undoped sample expressed per gram of carbon support is 942 m^2 gC^{-1} and the values obtained for the other samples decreased with an increase in the concentration of the alkali metal species added, the value being as much as 30% lower for the catalyst doped with 20 wt.% K. Comparison of the results for the Li, Na and Cs-doped samples with those for the sample with the equivalent K content of 10 wt.% show that the Cs carbonate has a stronger effect on the surface area than do Li, K or Na salts. This should be related to the larger size of the Cs^+ cation, its radius being about 2.5 times larger than that of the Li^+ cation; the Cs carbonate will therefore also occupy a larger volume. The BET results indicate that the alkali salts block access to the smaller pores of the carbon support, this giving a decrease in the apparent surface area. The total pore volume was measured for the undoped Pd/C and the 10 wt.% K-Pd/C and it was found that the K carbonate caused a decrease from 0.49 to 0.33 cm^3 g^{-1}; this decrease indicates that the K salt occupies a significant proportion of the volume of the pores. The BET surface area of the Pd powder was 20 m^2 g^{-1}; assuming that the Pd particles are spherical, this corresponds to an average Pd particle size of 25 nm.

We reported earlier [16] that the mean Pd particle sizes of the K-doped Pd/C samples with K contents of 0, 2 and 10 wt.% were all about 3.6 nm and the value did not change with K-doping, this indicating that the presence of K carbonate species does not bring about any sintering of the Pd particles. The results obtained from CO adsorption experiments for the same samples are demonstrated in Table 1, these showing that the CO chemisorption decreased by a factor of about 1.6 when 10 wt.% K was added. This can be related to a partial blockage of the Pd surface by a K salt or blockage of the pores in which the Pd particles are located. The CO adsorption data for the unpromoted Pd were used to calculate an average Pd particle size of 2.9 nm for this sample, a value comparable with that obtained by TEM. Fig. 2 shows the results of line-scanning EDS for the 10 wt.% K-Pd/C catalyst which demonstrate that the K ions of this sample are evenly distributed over the entire surface both the Pd and the C of the catalyst.
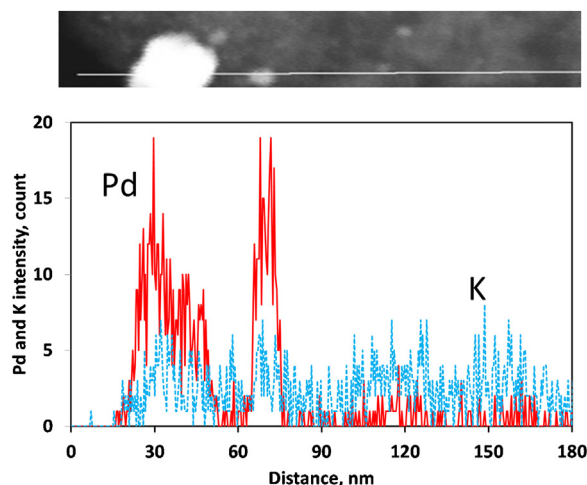
XRD measurements (Fig. 3) gave a very broad diffraction line corresponding to Pd(1 1 1) at about 40.1–40.2°, the level of the line-broadening confirming the high dispersion of the Pd. Diffraction peaks due to the presence of potassium bicarbonate crystallites were found for the 10 wt.% K-Pd/C catalyst but these were not observed for the 2 wt.% K-Pd/C sample; however, the latter result does not exclude the possibility that highly dispersed and hence X-ray amorphous potassium carbonate and/or bicarbonate species also exist in the samples with lower K loadings. That the bicarbonate was present on the samples despite the fact that the samples were prepared using the carbonate indicates that the interconversion of potassium carbonate and bicarbonate occurs readily under relatively mild conditions. In the absence of water, the samples most probably contain carbonate species but these species can readily be converted to bicarbonate in the presence of damp air:

$$K_2CO_3 + CO_2 + H_2O \leftrightarrow 2KHCO_3 \tag{1}$$

this reaction being reversible after removal of water, for example during the pretreatment of the samples before measurements (see Section 3.2.1).

The results of TOF-SIMS analysis of the 10 wt.% K–Pd/C catalyst shown in Fig. S1 and described in the Supplementary Material indicate that well-dispersed K-containing species are present in the sample and that large particles (2–7 μm) of K-carbonate and/or bicarbonate also exist. This may indicate that the used concentration of potassium salt exceeds a monolayer (saturation) value.
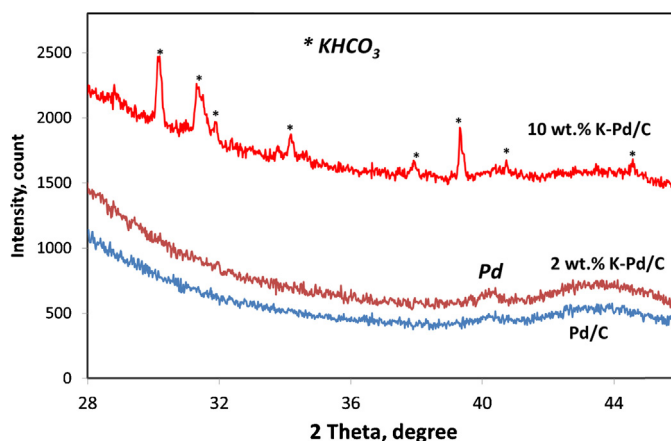

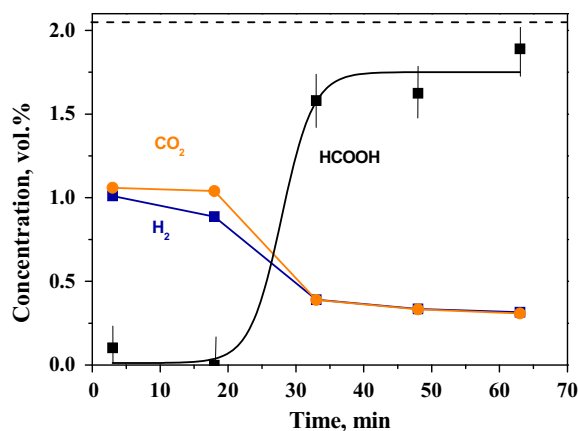**Fig. 3.** XRD pattern of the undoped and doped Pd/C catalysts (0, 2 and 10 wt.% K) after reduction.

Fig. 4. Concentrations of H_2, CO_2 and formic acid as a function of time over the reduced 10 K-Pd/C sample after a switch from a He flow to a formic acid/He flow at 333 K.

Fig. 5. The differences between the CO_2 and H_2 concentrations as a function of time after introduction of the formic acid to the 1 wt.% Pd/C catalyst with different contents of K ions at 333 K.

XPS examination of the samples was carried out to show whether or not there was any significant interaction between the Pd and the K species and the results for the undoped and K-doped Pd/C and Pd powder samples are summarised in Table S1. There was no shift in the binding energies of the Pd in either the oxidised or metallic forms when the K content was increased. The results also show that the ratio of the surface concentration of the oxidised form of Pd to the total concentration of Pd does not change noticeably with the addition of the K carbonate. We conclude that there is no significant interaction between the Pd and the K-containing species. This does not exclude the possibility that K-containing species are located either on the Pd nanoparticles in the form of islands or at the interface between the Pd and the support in a similar way to that proposed earlier by Zhu et al. [25] for a Na–Pt/TiO_2 system.

3.2. The effect of doping by alkali metal species on the catalytic performance of Pd/C

3.2.1. Establishment of the steady-state behaviour

It was found that all of the promoted catalysts exhibited a clearly seen unsteady-state period prior to the establishment of steady-state behaviour (see Section 3.2.2). Fig. 4 shows the results obtained with the 10 wt.% K-Pd/C sample for the decomposition of formic acid during the first hour of operation. Three specific features can be seen during this time, these being typical of the results obtained for all the K-doped samples examined. These are: (i) a greater initial rate of CO_2 evolution as compared to that of H_2; (ii) a greater initial consumption of formic acid compared to the quantities of products formed from the decomposition of the formic acid; and (iii) an initial decrease with time of the concentrations of CO_2 and H_2 (and hence of the rates of formation of these molecules compared with the steady-state values attained after 1 h of operation). If the stoichiometry of the formic acid decomposition reaction during the early stages of reaction was that of Eq. (2):

$$HCOOH \rightarrow H_2 + CO_2 \tag{2}$$

the volumes of H_2 and CO_2 produced would be expected to be the same. However, the results of Fig. 4 show that there is a difference between the CO_2 and H_2 concentrations as a function of time during the early stages of reaction; as it is shown in Fig. 5, similar behaviour was found in all the experiments carried out with the Pd/C sample doped with different concentrations of K species. It is therefore likely that reactions in addition to that of Eq. (2) take place in the early stages after the introduction of gaseous HCOOH to the K-doped materials and it is apparent that these changes are
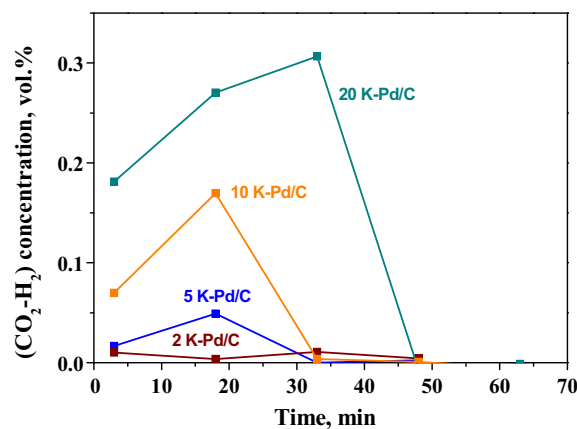
associated with reactions involving the K species added to the catalyst. Thus, reaction (3), involving the formation of formate species in place of the carbonate species initially present and takes place in parallel to the formic acid decomposition reaction (Eq. (2)) when the HCOOH is first introduced to a K-doped catalyst:

$$K_2CO_3 + 2HCOOH \rightarrow 2KHCOO + H_2O + CO_2 \tag{3}$$

The excess of CO_2 observed is thus formed as a result of reaction (3) and this amount can be quantified by integration of the areas under the curves of Fig. 5. Table 2 shows this excess quantity for the highest K^+ loadings. It also gives the corresponding values of the ratio of this excess to the K contents, $(CO_2–H_2)/K^+$. The values of the ratios are close to 0.5 and hence correspond approximately to the stoichiometry of reaction (3). The reaction of formic acid with a 10 wt.% K/C sample without any Pd gave only CO_2 as a product and the reaction ceased after about 20 min; in other words, only reaction (3) occurred on this sample and hence we conclude that reaction (3) can occur independently of the presence of Pd.

Table 2 also gives the quantities of formic acid adsorbed on the catalysts during the early stage of reaction as a function of the K content. This quantity was obtained by integration of curves of the percentage of adsorbed formic acid as a function of the operation time. This percentage was determined in each case from the difference between the total quantity of formic acid consumed and the quantity consumed in forming H_2 in the dehydrogenation reaction (Eq. (2)). It can be seen from the results in Table 2 that the amount of formic acid adsorbed increases with K content.

The final row of Table 2 shows the amounts of formic acid molecularly adsorbed ("condensed") on each of the catalysts after correction for the amounts converted to formate (Eq. (3)) and hydrogen (Eq. (2)). The values obtained for all the catalysts studied range from 0.16 to 0.31 $cm^3\,g^{-1}$. The volume of molecularly adsorbed formic acid is considerable and the values obtained approach the total pore volume of the carbon support of

Table 2
The difference between the amounts of CO_2 and H_2 evolved at 333 K during the interaction of formic acid with the undoped and K^+-doped Pd/C catalysts and the steady-state concentrations of adsorbed and condensed formic acid.

K content (wt.%)	0	10	20
$(CO_2–H_2)$ (mmol)	0	0.07	0.23
$(CO_2–H_2)/K^+$ (mol mol^{-1})	–	0.43	0.67
Volume of liquid HCOOH adsorbed/catalyst weight (cm^3 g^{-1})	0.16	0.29	0.52
Volume of liquid HCOOH condensed/catalyst weight (cm^3 g^{-1})	0.16	0.22	0.31

0.49 cm³ g⁻¹ determined for the undoped sample. From these studies, we conclude that the catalysts contain significant quantities of molecularly adsorbed formic acid as well as K formate in reaction conditions.

The results of Fig. 4 show that there is a significant decrease in the rate of the dehydrogenation reaction (shown by the rate of hydrogen production) with time of reaction. For the samples doped with alkali ions, CO is formed by the dehydration reaction with a very low selectivity (<0.5%, see Table 1). An inhibition by CO may contribute to the dynamic behaviour shown in Fig. 4 since it has been found (see Fig. S2) that the introduction of CO into the reaction mixture brought about a strong inhibition of formic acid decomposition for the 10 wt.% K-Pd/C catalyst in the same way that was observed previously for the undoped Pd/C sample [15].

In summary, adsorption and other related processes take place during the period before the reaction system attains a steady state. The formic acid is consumed in three different ways: a certain fraction decomposes into H_2 and CO_2, the decomposition rate decreasing with time probably as a result of poisoning by traces of CO formed in a parallel dehydration reaction; a significant fraction is condensed in the pores of catalyst; and another fraction reacts with K carbonate to form K formate, this process being accompanied by the evolution of CO_2 in excess of the amount of H_2 formed. We therefore conclude that at the steady-state, the pores of the active catalyst contain K formate and formic acid in a liquid-like phase. We cannot exclude the possibility that there is also water condensed in the pores, this either having been formed in reaction (3) or having been present as an impurity in the formic acid reactant (<2%).

3.2.2. Steady state results

We have previously shown data for the steady-state conversion of formic acid (i.e. reaction after approximately 1 h) as a function of temperature for the undoped and K-doped samples [16] and these results are summarised in Table 1 in the form of T_{50}, the temperature required to give 50% conversion of the formic acid, as a function of the wt.% K added. In all cases, the formic acid was converted almost exclusively to hydrogen and CO_2, with only minor quantities of CO and H_2O are being formed. The value of T_{50} decreases with increasing K content up to 10 wt.%, the latter corresponding to a K/Pd mole ratio of 27; a further increase of the K content up to 20 wt.% leads to a slight increase in T_{50}. It would therefore appear that the sample with 10 wt.% K corresponds to approximately the optimum level of the K carbonate promoter. While the undoped sample gave a conversion about 50% with 98.9% selectivity to hydrogen at 385 K, the sample containing 10 wt.% K gave a conversion of 50% with 99.8% selectivity at a temperature of 340 K, some 45 K lower.

An experiment lasting 22 h at 343 K was also carried out using the 10 wt.% K-doped Pd/C catalyst (Fig. S3). The conversion after the first hour of operation was about 66% and this value decreased only slightly to about 64% during the experiment; the hydrogen selectivity remained above 99.8% throughout the experiment, this corresponding to a CO content of less than 30 ppm a value making this system suitable for fuel cell applications.

Fig. 6 shows results obtained for samples prepared from the Pd/C material using salts of the other alkali metals as dopants, the concentration of each salt being chosen to correspond to the optimum alkali metal/Pd molar ratio of 27 found for potassium (10 wt.%). It is seen that doping with K carbonate had the most marked effect on the measured conversions and that the results for the addition of Cs carbonate were very similar. The Na and Li dopants were less effective. The values of T_{50} and the corresponding hydrogen selectivities for these catalysts are also shown in Table 1: for the K-doped Pd/C sample, T_{50} was about 340 K and the corresponding values for
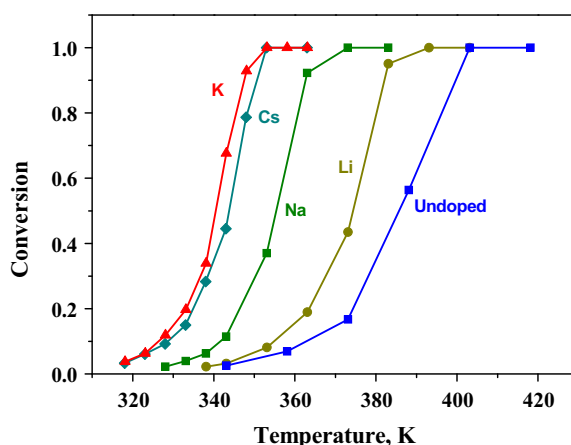
Fig. 6. Conversion of formic acid on the 1 wt.% Pd/C catalyst doped with various alkali metal ions; all were present at a 27:1 mole ratio relative to the Pd (for the K-doped sample this ratio corresponded to 10 wt.% of K).

the samples doped with Cs, Na and Li species were 344, 355 and 374 K, respectively. The hydrogen selectivities determined for 50% conversions were higher for all the doped materials than for the undoped sample. These selectivities were also higher for all the samples than those calculated assuming the occurrence of equilibrium in the WGS reaction. For example, with the 10 wt.% K-doped sample, the experimental value was 99.8% while the corresponding equilibrium value was calculated to be 99.1%.

All the alkali metal species gave promotion of the Pd/C catalyst, the order of the activity measured for samples with the same metal ion to Pd ratios being K ≥ Cs > Na > Li > undoped (Fig. 6, Table 1). Thus, it appears that the cations with the largest radii have the strongest effect on the catalytic activity. There is also an optimum concentration of alkali metal in the catalyst (Table 1) and this is probably related to the limited solubility of the alkali metal formates present in the liquid condensed in the pores of the catalysts, although it could to some extent be due to blockage of the smaller pores of the support with higher contents of alkali dopant. Hence, a correlation may exist between the solubility of the alkali metal formate [30] and the activity of the promoted catalyst in formic acid decomposition; this will be discussed further below.

The undoped and 10 wt.% K-doped Pd/C catalysts were also tested for their activities in the WGS reaction and the results are shown in Fig. 7. The undoped Pd/C catalyst had almost negligible activity for this reaction at temperatures lower than 573 K. However, the addition of K ions gave a very remarkable increase (by a factor of more than 40) in the activity, the sample containing
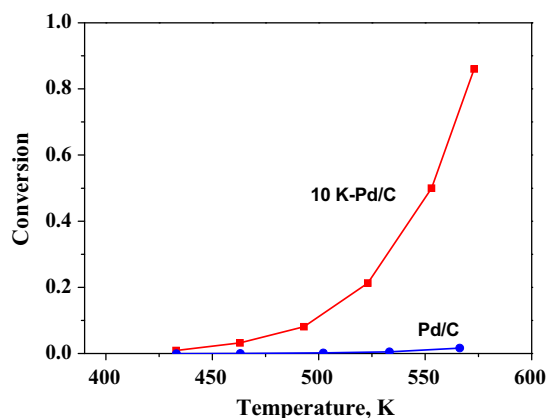
Fig. 7. Conversion of CO in the water–gas shift reaction on the 1 wt.% Pd/C catalyst, with and without addition of 10 wt.% K.
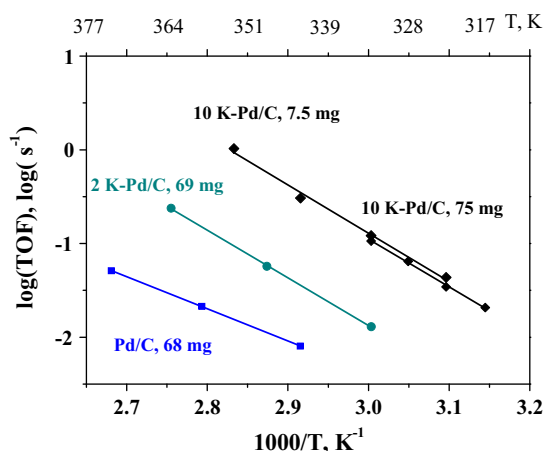
Fig. 8. Arrhenius plots of the TOF values for the formic acid decomposition on the 1 wt.% Pd/C sample without K and with 2 and 10 wt.% of K.

10 wt.% K giving reaction at a temperature as low as about 433 K. Generally, formic acid decomposed to give hydrogen on the K-doped Pd catalyst at temperatures that were about 170 K lower than those shown in Fig. 7 for the WGS reaction. Hence, it is probable that the WGS reaction is not at equilibrium under the conditions used for formic acid decomposition. The results reported above are all consistent with CO_2 and H_2 being the primary products of the formic acid decomposition reaction over K-doped Pd/C catalysts and the conclusion that these materials are very selective for dehydrogenation.

The concentrations of the surface Pd sites for the K-doped and undoped samples were calculated on the basis of the CO chemisorption measurements (Pd dispersion, Table 1) and the corresponding TOFs for formic acid decomposition were calculated. The TOF value at 353 K for the undoped Pd/C catalyst was $0.015\,s^{-1}$ while doping of the Pd/C catalyst with 10 wt.% K led to a considerable increase of the TOF, by a factor of up to 65, giving a TOF value of $1\,s^{-1}$. Several of the sets of results obtained are plotted as log(TOF) versus reciprocal temperature in Fig. 8 and the values of apparent activation energy and the pre-exponential factors determined from such plots for the samples are given in Table 1. There is a very significant difference between the apparent activation energies obtained for all the K-doped samples and that for the undoped sample: the activation energy for the undoped catalyst was $66\,kJ\,mol^{-1}$ while the values obtained for the doped samples are in the range 87–$98\,kJ\,mol^{-1}$. Significantly increased activation energies were also observed for the samples doped with Li, Na and Cs: the values were also in the same range 88–$99\,kJ\,mol^{-1}$ (Table 1). These increases in the values of the activation energies were compensated by very remarkable increases in the apparent pre-exponential factors, there being increases of 3.4–6.3 orders of magnitude; as seen in Table 1.

It is evident, that the increase in the pre-exponential factor on doping with K is related to the amount added to the catalyst. For example, although the activation energy for the reaction increased on the addition of even a small amount of K (2 wt.%) to give approximately the same value as that for the 10 wt.% K sample, the value of the pre-exponential factor was significantly lower for the lower quantity of K. Despite this change in the pre-exponential factor, there was no significant change in the concentration of the surface Pd sites, as determined by CO chemisorption, or in the Pd particle mean size, determined by TEM as discussed above. Hence, we conclude that the rate of the reaction is not only determined by the concentration of Pd sites on the catalyst but either by the number of K^+ species or by the number of formate anions in the liquid phase in the pores corresponding to these species. The latter is the
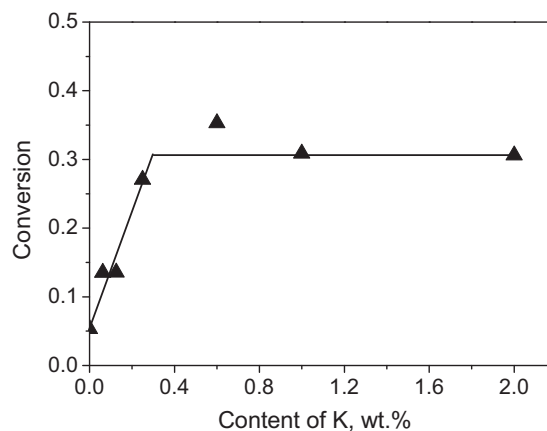
more likely explanation. We return to this point in the discussion section.

3.3. The effect of doping Pd powder with K ions

A series of experiments were carried out using unsupported Pd powder doped with different loadings of potassium ions to examine whether or not the carbon support is essential in relation to the doping effects described above for the K-doped Pd/C catalysts. For these samples, the unsteady-state period was very short and could not be examined adequately in our experimental system. Fig. 9 shows the steady-state conversions of such samples as a function of the K content for the formic acid decomposition reaction at 353 K. It can be seen that the conversion increased by a factor of up to 6 times for K concentrations up to about 0.3 wt.% as compared with that for the undoped sample but that the conversion then reached a plateau value with further addition of K. The selectivity values at 50% conversion and temperature of 356–404 K were in the range of 99.1–99.5%.

Arrhenius plots of the TOF values calculated from the conversion data for the undoped and some K-doped Pd powders are shown in Fig. 10. For the undoped Pd powder, the TOF value was equal to $0.013\,s^{-1}$ at 353 K and the apparent activation energy was $60\,kJ\,mol^{-1}$; values that are quite similar to those obtained for the undoped Pd/C catalyst. Following doping with K carbonate, the activity increased significantly and the activation energy increased
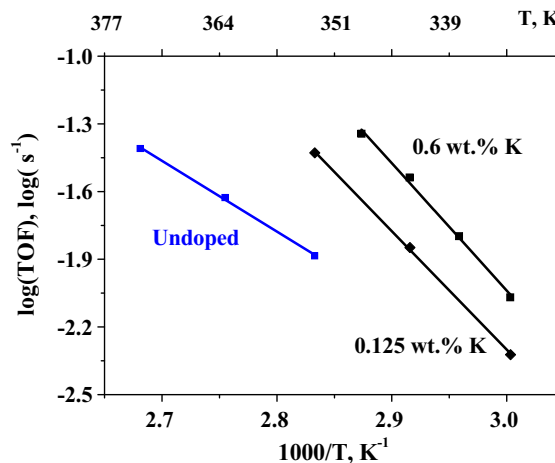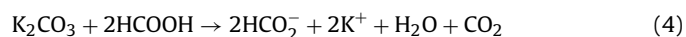

Fig. 9. Effect of K doping on the conversion of formic acid in the decomposition over a Pd powder at 353 K.

Fig. 10. Arrhenius plots for the TOF values for the formic acid decomposition on a Pd powder with and without added K.

to 100–108 kJ mol^{-1}. It is therefore probable that a change of the mechanism for the decomposition reaction on the Pd powder has taken place as a result of doping with the K containing salt that is similar to that described above for the Pd/C catalyst, this again being due to the presence of K formate in a condensed liquid layer present in the pores of the Pd crystallites. It should be noted, however, that the relative change of the reaction rate provided by K-doping is much smaller for the Pd powder than for the C-supported samples. This can be related to the larger pore sizes in the Pd powder as compared to those in the Pd/C samples.

4. Discussion

The results presented above show that the presence of alkali metal ions causes a very significant change in the behaviour of a Pd/C catalyst in formic acid decomposition. All the observations can be explained by the following sequence of reactions, all of which occur in a liquid-like "solution" within the pores of the Pd/C catalyst:

$$K_2CO_3 + 2HCOOH \rightarrow 2HCO_2^- + 2K^+ + H_2O + CO_2 \qquad (4)$$

$$HCOOH \leftrightarrow H^+ + HCO_2^- \qquad (5)$$

$$HCO_2^- + Pd \rightarrow PdH + CO_2 + e^- \qquad (6)$$

$$H^+ + Pd + e^- \rightarrow PdH \qquad (7)$$

$$2PdH \leftrightarrow 2Pd + H_2 \qquad (8)$$

Formate ions are initially generated in the pores by reaction (4), as was discussed above in Section 3.2.1, and these are stabilised by the presence of the K$^+$ ions. (For convenience, the cation included in Eq. (4) is shown as K$^+$ but equivalent steps apply to all the other cations; when impregnation was carried out with Li formate, the formate had probably been converted to carbonate during pre-treatment of the catalyst.) The dissociation of the formic acid also present in the solution takes place according to Eq. (5) and gives rise to further formate ions as well as to hydrogen ions. The resultant situation is akin to that of a buffer solution (a term normally associated with aqueous solutions) for which the following equation holds:

$$K_d = a_H + a_{HCOO^-} \qquad (9)$$

where a_{H^+} is the activity of the hydrogen ion in the solution, a_{HCOO^-} is the activity of the formate ion and K_d is the dissociation constant of formic acid. As the dissociation constant for the weak acid, HCOOH, is very small, the activity of the formate anions is approximately equal to the activity of the counter-cation of alkali metal. The consequence is that the activity of the formate ions in the pores remains constant even though they are continuously reacting in a series of steps to produce CO$_2$ and H$_2$ as shown in Eqs. (6)–(8). In step (6), the formate anion transfers an electron (e$^-$) to the Pd, forming gaseous CO$_2$ and a hydrogen atom adsorbed on Pd surface. In parallel to this step, a proton accepts the electron from the Pd, this also giving rise to an adsorbed hydrogen atom (step (7)). The two adsorbed hydrogen atoms then associate and desorb as a hydrogen molecule (step (8)). Generally, at the studied conditions equilibrium exists between gas phase hydrogen and hydrogen adsorbed on Pd.

To complete the cycle and maintain the stationary state existing in the pores of the catalyst, a further molecule of formic acid dissociates (Eq. (5)), the charge balance being maintained and the concentration of formate ions was remaining equal to that of K$^+$ ions. The all-over rate-determining step is thus probably the reaction shown in Eq. (6) as a strong dependence of the reaction rate on the potassium (formate) concentration exists in a certain range (Figs. 8 and 10). The adsorbed hydrogen can inhibit step 6

for decomposition of formate ions and this should be taken into account for the process development. Additionally, at high concentrations of alkali metal salts their solubility in a liquid condensed in the pores should be taken into account. This follows from the TOF-SIMS data indicating the presence of large particles of K carbonates in the 10 wt.% K–Pd/C sample. Thus, bulk insoluble particles of alkali metals formate may also exist in the reaction conditions for the catalysts with high concentrations of dopants.

The sequence of reactions presented is supported by the observation reported above that a significant fraction of the formic acid is condensed in the pores of the catalysts during the early stages of reaction after introducing formic acid to the samples and relatively small dependence of the rate of reaction on the formic acid partial pressure. Other research groups have reported that a condensed formic acid can be observed by "in situ" infrared (IR) spectroscopy on SiO$_2$-based catalysts [21,31,32] under conditions close to ours. In all these cases, the IR results obtained showed the presence of a stretching vibration of a hydrogen-bonded carbonyl group (C=O) at a wavenumber of 1715–1735 cm^{-1}, this being shifted with respect to the corresponding band for gaseous formic acid (1770–1790 cm^{-1}) and confirming the existence of formic acid in a condensed phase.

We have shown earlier [16] that the catalytic behaviour of a composite catalyst bed consisting of a sample of the Pd/C catalyst separated by quartz wool from a K/C sample was close to that of the pure Pd/C catalyst; however, if the Pd/C catalyst was physically mixed with the K/C sample, a considerably improved activity, close to that observed for the Pd/C catalyst impregnated with K carbonate, was reached. These results indicate that K-containing species are very mobile under the reaction conditions as a result of the presence of the condensed liquid phase; this mobility was confirmed by EDS measurements on the used catalysts that showed the presence of potassium on the Pd/C component of the mixture.

The concentration of formate ions in aqueous formic acid is very small as its dissociation constant is very small. In contrast, dissolved alkali metal formates are completely dissociated in water or in formic acid solutions. Although the situation will be different if the solvent is rich in formic acid as in our catalysts, the formate ion concentration in the K formate solution in the pores of our catalysts is likely to be several orders of magnitude greater than in the absence of K formate. In the absence of K formate, the rate of decomposition of the low concentration of formate ions present will therefore be negligible compared with the decomposition of vapour phase molecular formic acid by the more usual catalytic route. Hence, for the K/Pd/C reaction system discussed here the mobile formate ions present in the condensed phase of formic acid in the pores of the support material (and stabilised by the cations of the alkali metal) are the active species that participate in the catalytic reaction.

We have attempted to use diffuse reflectance infrared spectroscopy (DRIFTS) to the Pd/C catalysts, however, these attempts were unsuccessful because of complete absorption of the incoming infrared energy by the samples. In contrast, our infrared spectroscopic "in situ" study with K-doped and undoped Pd/SiO$_2$ catalysts gave some important results [33,34]. They fully confirmed the reported mechanism of K-doping. These studies showed the evidence of condensed formic acid in the pores for the doped and undoped samples and the presence of formate ions only in the doped sample. For the Pd/SiO$_2$ a catalytic promotion effect of potassium carbonate was similar to that observed for the Pd/C sample. These novel results will be discussed in detail in a subsequent publication [34].

A reaction mechanism consistent with our results is shown schematically in Fig. 11. Formic acid decomposition takes place mainly via the decomposition of formate ions on the surface of Pd crystallites within the pores of the support. These ions are dissolved
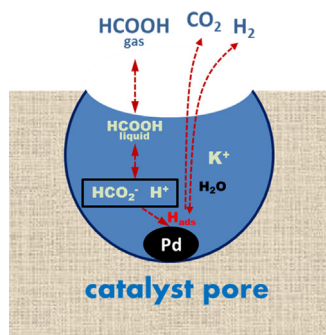
Fig. 11. Schematic representation of the HCOOH decomposition over a Pd nanoparticle located in a condensed liquid in the pore of the C support of the Pd/C catalyst. (Electron transfer takes place on the Pd.)

in a condensed liquid. The contribution of vapour-phase decomposition is negligible as the rate of this reaction is much lower than the rate of the liquid phase decomposition, the proportion of the Pd existing on the external surface of the support and not immersed in the condensed liquid being very small.

For the unsupported Pd powder, the promotional effect was much lower than that for the K-doped Pd/C samples. This difference is probably the result of the existence of larger pores and of the consequent significant decrease in the Pd/liquid interface as compared to that in the supported catalyst. The situation for the unsupported material is shown schematically in Fig. 12; the condensed liquid is now most probably located in the region of contact between the Pd crystallites and the uncovered Pd surface is much greater. Hence, the promotional effect due to reaction at the Pd/solution interface is much less significant with these samples.

Hu et al. [35], on the basis of density functional calculations (DFT) calculations and experimental studies [12], suggested that the mechanisms of formic acid decomposition on noble metals in the vapour and aqueous phases are different. They proposed that this difference is due to the presence of formate ions in the aqueous-phase and this is in agreement with what we propose above. These authors showed that the decomposition of formate ions takes place on the surface of Pd(1 1 1) by spontaneous dissociation, forming adsorbed hydrogen and CO_2. They noted that the interaction of the CO_2 with the metal surface is negligible.

The decomposition of unsupported bulk alkali metal formates normally takes place at temperatures above 573 K [36]. The formate ions in the condensed liquid present in our catalysts decompose on Pd to give hydrogen and CO_2 at much lower reaction temperature (333–353 K). At the reaction conditions used in this work at least a part of the water formed in reaction (3) remains in the pores of the catalysts. Water is also formed in the parallel dehydration reaction of formic acid to give CO and H_2O even though the selectivity of this reaction is very low (<0.5%) (Table 1) and some water may also

originate from impurity in the formic acid reactant. Hence, the water constituent in the pores may contribute in some way or another to the behaviour of the catalysts studied here, the condensed formic acid/water solution providing easy access of the formate ions to the active Pd sites. Some papers in the literature indicate clearly that water is also necessary for low temperature formate decomposition. For example, Jacobs et al. [27] have demonstrated that water promotes the decomposition of formate species over Pt on oxidic supports. Wang et al. [14] have also shown that water is necessary for formate decomposition on a Pd/C catalyst in the liquid phase as no decomposition of a formic acid/formate mixture took place when the water was substituted by tetrahydrofuran. Wiener et al. [23] previously confirmed the need for water for formate decomposition in the liquid phase in the presence of a Pd/C catalyst by carrying out kinetic isotope effect studies.

We also cannot exclude the possibility that bicarbonate ions are present in small concentrations in the pores of the catalyst, these being formed mainly in the equilibrium [37]:

$$HCO_2^- + H_2O \leftrightarrow H_2 + HCO_3^- \qquad (9)$$

Further, we cannot exclude the possibility that water present in the pores forms carbonic acid with CO_2 and that related species also contribute to the reaction.

Ojeda and Iglesia [17] have reported very high values of TOF (0.6 s^{-1} at 353 K) for the vapour phase decomposition of formic acid over Au/Al$_2$O$_3$ catalysts. However, the best results for hydrogen production reported to date have been obtained from the liquid phase decomposition of formic acid using homogeneous catalysts based on complexes of Rh (TOF = 0.6 s^{-1} at 298 K) [38], Ru (TOF = 1 s^{-1} at 323 K) [39,40], Fe (TOF = 2.6 s^{-1} at 353 K) [24] or Ir (TOF = 3.9 s^{-1} at 363 K) [41]. The highest activities obtained in our work, with a TOF value of 1 s^{-1} at 353 K and excellent hydrogen selectivity (>99.8%), are comparable to those for the decomposition of aqueous formic acid solutions using homogeneous catalysts. It should be noticed that experiments on formic acid decomposition in the liquid phase have often been performed in the presence of water, different amines or formates, all of which promote the reaction activity.

The discussion above has been based largely on a discussion of the use of K carbonate as promoter but similar arguments also apply to the promotion observed with the other alkali carbonate promoters, the activation energy for the decomposition of the formate ions formed being approximately the same for all the alkali metal cations (Table 1), the main differences being probably due to differences in the solubilities of the corresponding formates [30] in the pores of the Pd/C catalyst used. It is also interesting to note that the promotional effect was found for the water–gas shift reaction although that reaction only proceeded at significantly higher temperatures. This allows us to conclude that the formate ions formed in the presence of alkali cations cannot easily decompose to form CO and water at the temperatures used for the formic acid decomposition, thus favouring high selectivities to hydrogen production.

5. Conclusions

We report the results that show a considerable promotional effect of alkali metal salts on the rate of hydrogen formation from formic acid decomposition over a 1 wt.% Pd/C catalyst. The effect of alkali metal ions addition to the catalyst followed the order K ≥ Cs > Na > Li. A sample containing 10 wt.% K provided hydrogen production almost free of CO (<30 ppm) and the steady-state turnover frequency of this sample at 353 K was 65 times higher than that for the undoped material. The early stages of the decomposition of the formic acid were studied with the K-Pd/C catalysts and it was found that a significant proportion of the HCOOH that reacted
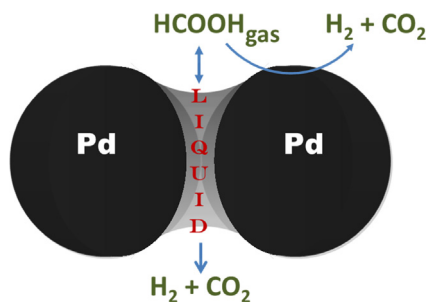

Fig. 12. Schematic representation of the vapour and liquid phase HCOOH decomposition over 2 Pd crystallites of the unsupported Pd powder. (The liquid represents a mixture of HCO$_2^-$, K$^+$ and H$^+$ ions dissolved in a condensed HCOOH/H$_2$O phase)

during this period was condensed on the K-doped Pd/C catalyst while another part reacted with carbonate species to form formate ions dissolved in the condensed formic acid/water mixture. Unsupported Pd powder doped with K^+ ions exhibited a lower but still a well-defined promotional effect and this implies that the formate ions dissolved in condensed liquid are important in this case also. Based on all the results obtained, a reaction mechanism involving formate ion decomposition to give CO_2 and H_2 is proposed. The mobility of the formate ions in condensed liquid significantly increases the probability of contact of these ions with a Pd catalytic site and therefore accelerates the decomposition of the formic acid, this being an essential factor in improving the all-over reaction rate. A similar explanation applies to the promotional effect observed for the water–gas shift reaction over the same catalysts, even though the activities for this reaction are much lower.

Acknowledgements

Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at http://dx.doi.org/10.1016/j.apcatb.2014.05.004.

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